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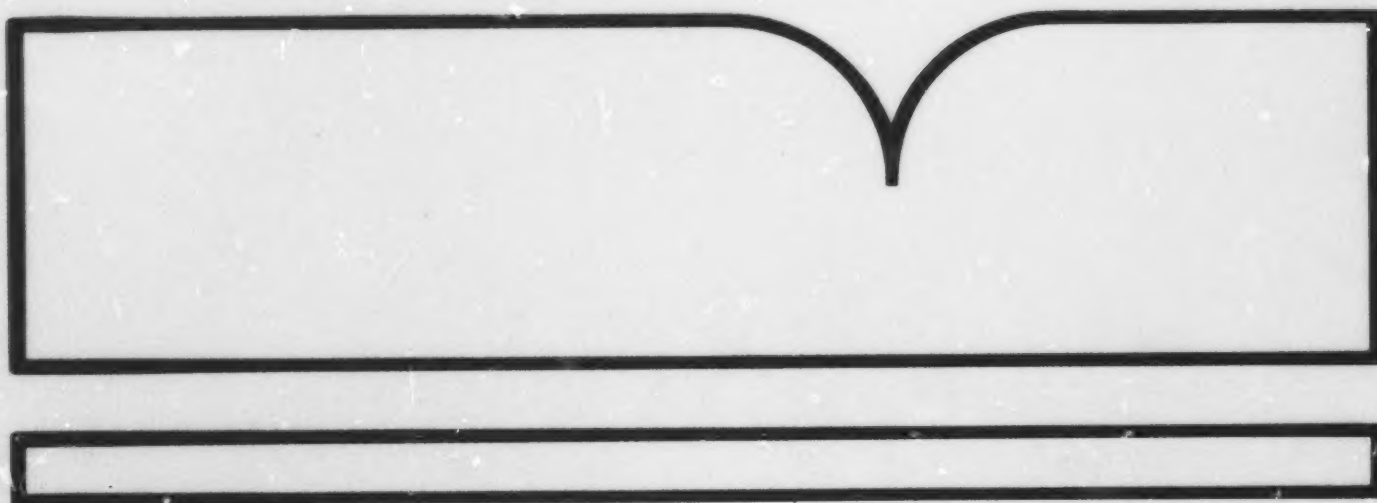
Biogeochemistry of Aluminum in McDonalds
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Biogeochemistry of Aluminum in McDonalds Branch Watershed, New Jersey Pine Barrens

R. S. TURNER, A. H. JOHNSON, AND D. WANG

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Biogeochemistry of Aluminum in McDonalds Branch Watershed, New Jersey Pine Barrens¹

R. S. TURNER, A. H. JOHNSON, AND D. WANG²

ABSTRACT

Aluminum concentrations, fluxes, and storage were measured in the vegetation, forest floor, and acid, sandy mineral soil of a forested watershed in the New Jersey Pine Barrens. Volume-weighted mean Al concentrations in solution increased as water passed through the upland ecosystem, from 0.012 mg L⁻¹ in bulk precipitation to 0.14 mg L⁻¹ in throughfall to 0.45 mg L⁻¹ in E horizon mineral soil, 0.60 mg L⁻¹ in the B horizon, and 0.73 mg L⁻¹ in the C horizon. Weighted mean Al concentration of the stream water was 0.15 mg L⁻¹. Solution Al concentrations in different compartments of the ecosystem were related to the magnitude of moisture flux, dissolved organic carbon concentration, and pH. Soil solution and stream water Al concentrations were high in the winter and spring and low in the summer and fall, inversely following solution pH. Soil solution and stream pH were independent of precipitation pH because of internal control of H⁺ concentration by the soil and an apparent 0.5-yr time lag in flushing of atmospherically deposited acids through the soil. Aluminum was partitioned strongly into the lower mineral soil horizons, but large stores of potentially labile Al were found in the upper mineral horizons and forest floor. Standing vegetation represented a relatively small pool of Al but cycled substantial amounts of Al between mineral soil and the forest floor.

Additional Index Words: acid precipitation, budgets, forest soils, lysimeters.

Turner, R. S., A. H. Johnson, and D. Wang. 1985. Biogeochemistry of aluminum in McDonalds Branch Watershed, New Jersey. *J. Environ. Qual.* 14:314-323.

Mobilization of aluminum in terrestrial and aquatic ecosystems has been identified as a potentially detrimental result of acid precipitation. Cronan and Schofield (1979) compared solution values of H⁺ and Al (total) in the balsam-fir (*Abies balsamea*, Mill.) zone of the White Mountains in New Hampshire with values obtained by Ugolini et al. (1977) for a comparable subalpine zone at Findley Lake, WA. Findley Lake is in an area little affected by acid deposition, and solution chemistry there followed the organic acid-dependent pattern of Al mobilization in the canopy, litter, and upper mineral soils and precipitation of the Al in the illuvial B2 horizon. Solution chemistry data from the acid-precipitation system in New Hampshire showed

that dissolved Al reached high concentrations in the forest floor, increased in the B2 horizon, and had highest concentrations in spring water. The high Al concentrations could be accounted for by gibbsite dissolution as a result of the low pH of the soil solution. Cronan and Schofield (1979) postulated a linkage between acid precipitation, high Al concentrations in soil solution and high levels in lake water, and toxic effects on fish in acidified lakes of the Adirondack region of New York. Driscoll et al. (1980) also linked toxic effects in fish to seasonally high levels of dissolved inorganic Al in acidified waters of the Adirondacks.

Ulrich et al. (1980) related acid precipitation and internal soil processes to seasonally high Al levels in the soil solution and dieback of beech roots (*Fagus sylvatica* L.), especially in dry years. They also reported a long-term (1966-1979) increase in Al concentration in equilibrium soil solution and presumed that "...the buffer reaction has proceeded deeper into the soil."

Wiklander (1975) reported that exchangeable Al could be very high in the O horizon of Scandinavian soils and that it could be leached readily by acid precipitation.

Johnson (1979) and Johnson et al. (1981) hypothesized that at Hubbard Brook, NH, neutralization of strong acids from precipitation was accomplished in a two-step process. Hydrogen ions were neutralized initially by rapid dissolution of Al salts, primarily in the soil zone, followed by slower neutralization of H⁺ and

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Al acidity by chemical weathering of primary silicate minerals. Reaction rates were such that, where residence times were short (low-order watersheds with rapid throughflow), solutions were acidic and had high Al concentrations, whereas after sufficient time had elapsed (e.g., in streams of third order or above), Al acidity had been neutralized and pH was > 5.2 . Even during the spring runoff, only a very short channel distance (< 100 m) was required before free inorganic monomeric Al fell well below toxic levels for fish.

Numerous other studies (Hutchinson and Havas, 1980; Drablos and Tollan, 1980; Overrein et al., 1981) also showed that Al is mobilized in many forms and complexes, depending on pH, types of organic compounds, and other ions in solution. Mobilization or precipitation of Al is dependent on primary parent minerals and secondary soil minerals present and on reaction rates and contact time between solution and substrate. Because the mobility of Al is tied to so many variables, Al fluxes and stores in natural systems might be expected to vary greatly in space and time.

This paper summarizes aluminum fluxes and storage in a forested watershed in the New Jersey Pine Barrens. Precipitation, throughfall, soil moisture in three horizons, and stream water were studied to monitor Al movement through the system. Data on pH, organic concentrations, and water fluxes are presented because they appeared to exert some control over Al solubility. Other parameters that may control Al mobilization, such as Al speciation and SO_4^{2-} concentration, were not determined.

MATERIALS AND METHODS

A brief description of the study site and methods follows. More detail can be found in Turner (1983) and Wang (1984).

Study Site

The McDonalds Branch Watershed is a 6.0-km² forested area in Lebanon State Forest in the New Jersey Pine Barrens. It is underlain by sands and gravels of the Miocene Cohamsey Formation. The basin is in the higher elevations (35–65 m) of a coastal plain that has lain above sea level for the past five million years and which has been subjected to extensive fluvial and aeolian erosion and local redeposition (Rhodehamel, 1979). Relief is slight; only small areas have slopes as great as 10%.

Upland sandy soils are excessively drained, rapidly permeable, highly leached Quartzipsamments. They are extremely acid (pH 3.4–4.6), have a very low cation exchange capacity (0–3 cmol (+) kg⁻¹), and very low base saturation (0–20%) (Markley, 1979; Douglas and Trela, 1979). Kaolinite, Al-interlayered vermiculite and smectite, and gibbsite are present, generally increasing in abundance with depth in the soil profile (Douglas and Trela, 1979). Lowland mineral soils are spodic Quartzipsamments having physical and chemical characteristics similar to the upland soils, except that they have a seasonally high water table. Bordering the stream, histosols (muck and peat) overlie the Cohamsey sands.

Except for direct precipitation on the stream and contiguous wetlands, virtually all water reaching the stream percolates through the sandy soil and shallow groundwater aquifer. The lack of exchangeable ions and weatherable minerals in the soil and geologic substrata is reflected in the water chemistry. Ground and stream waters are extremely soft (15–35 mg L⁻¹ total dissolved solids [TDS]) and have a mixed-cation-sulfate composition (USGS, 1981; Means et al., 1981).

Soil, bog, and stream waters often are colored yellow or brown as a result of dissolved organic matter concentrations. Essentially all of this material passes through a 1.0- μm membrane filter, and much of the color remains in solution after passing through a 0.01- μm mem-

brane filter. The organic matter retained by the filter was not quantified or identified.

Canopy vegetation in the uplands is dominated by pitch pine and shortleaf pine (*Pinus rigida* Mill. and *P. echinata* Mill.) and oaks including black, blackjack, white, and post (*Quercus velutina* Lam., *Q. marilandica* Muench., *Q. alba* L., and *Q. stellata* Wang., respectively). The understory is largely lowbush blueberry (*Vaccinium vacillans* Kalm.), black huckleberry (*Gaylussacia baccata* Wang.) and, in some places, scrub oak (*Q. ilicifolia* Wang.). Many of the pines and most of the oaks are of sprout origin after cutting or fire. Wildfire and prescribed burning have played major roles in determining the species composition and structure of the upland forests (Little, 1979).

Lowland communities include hardwood swamps of red maple (*Acer rubrum* L.) and black gum (*Nyssa sylvatica* Marsh.) and nearly monospecific swamps of white cedar (*Chamaecyparis thyoides* L.). Both have an ericaceous understory and thick mats of sphagnum moss. A transitional community, the pitch pine lowland, occupies extensive areas between upland forests and wetlands. Pitch pine dominates the canopy, and red maple and black gum are also present. The ground is covered densely with many species of shrubs; sheep laurel (*Kalmia angustifolia* L.), leather leaf (*Chamaedaphne calyculata* Moench.), highbush blueberry (*V. corymbosum* L.), and black huckleberry are most common.

Watershed Input-Output

Bulk precipitation samples were obtained for chemical analyses using three polyethylene funnel-type collectors mounted in a configuration similar to that described by Likens et al. (1977). Snow was collected in a plastic bucket, melted in the laboratory, and then treated like other precipitation samples. Throughfall samples were collected under black oak, pitch pine, white cedar, and red maple/black gum canopies in four funnel collectors similar to the bulk precipitation collectors.

Precipitation input volume was measured using a network of 10 gauges in four locations within the watershed. Collectors included plastic-wedge gauges, wedge gauges having vapor traps, a tipping-bucket gauge, three funnel collectors with vapor traps, and the snow bucket. Throughfall depth (mm) was calculated from the volume collected in the funnel collectors. Measured precipitation did not vary systematically among collectors within the watershed, and generally was consistent with amounts collected at Lebanon State Forest Headquarters and at the NOAA station at Pemberton, NJ (5- and 16-km distance, respectively).

Surface-water samples were collected in polyethylene bottles from the stream just above the U.S. Geological Survey gauging station weir and, for a one year period, from pools in the cedar and hardwood swamps.

Soil Moisture

Soil water was sampled using 60 lysimeters of three types in Lake-wood and Evesboro soils at four upland locations within the watershed. Twenty-four plexiglass zero-tension, trough lysimeters (modified from Jordan [1968]), 20 aluminum-plate tension lysimeters (80 kPa, after Cole [1958]), and 16 funnel lysimeters (10-cm diam polyethylene funnels filled with acid-washed coarse sand) collected soil moisture from 10-cm (E/A2 horizon), 30-cm (B horizon), 1-m, 1.5-m, and 2-m (C horizon) depths. Six PVC tubes (4.5-cm inside diam. and 2 m long) were cut, shaped, sealed in a point, perforated in the lower meter with 0.5-mm holes, and installed in the cedar bog and hardwood swamp histosols and in the lowland Lakehurst mineral soils to sample lowland pore water.

Soil-moisture flux in the uplands was estimated using a one-dimensional box model (Wang, 1984) that could be driven by available environmental data. Input included daily mean temperature, daily precipitation, soil bulk density for 10-cm intervals to 1-m depth, and soil-moisture content at field capacity and at saturation. Using a time step of 1 d, the model successively added precipitation, subtracted evapotranspiration for leaves, litter, and soil and estimated excess water leached via saturated and unsaturated flows. Output was the flux of water in millimeters predicted to percolate past 10-cm, 30-cm, and 1-m depths. The model was calibrated using Pine Barrens soil-moisture data of Lull (1956), along with daily temperature and precipitation data. It was then run for each collection period in this study.

Correlation between volume collected by the lysimeters and leachate volume predicted by the model was high (r up to 0.99; variability was as high within lysimeter types as between lysimeter types), indicating that event and seasonal trends were realistic, but absolute volumes of water moving through the soil could not be verified with any of the lysimeters used. The predicted volume fluxes were used in calculating soil Al fluxes in lieu of more reliable data.

Vegetation

Allometric relationships from the studies of Whittaker and Woodwell (1968) and Woodwell et al. (1975) were applied in the McDonalds Branch watershed to predict biomass and standing-Al pools (Wang, 1984). For this study, three 20- by 20-m plots were sampled for diameter data from which 1979 biomass was calculated for the tree species present. To estimate net biomass increment over time, diameters measured from increment cores for the same trees were used to calculate 1969 biomass. The shrub subcompartment was sampled by harvesting completely ten 1- by 1-m plots and five 10- by 10-m plots for small (< 2.5 cm) and large shrubs, respectively.

Samples of stemwood, stembark, branches, twigs, current-year needles or leaves, and old needles were taken from each tree species, and whole shrubs were taken for tissue analyses ($n = 2$ to 10). Samples were oven dried (70°C) and ground; 1 g was dry ashed and then digested in HCl for analysis, following the procedure of Likens and Bormann (1970). (Subsequent tissue analyses using total (HF-HCl) digestion suggest that the above procedure may underestimate Al concentrations by up to 40%).

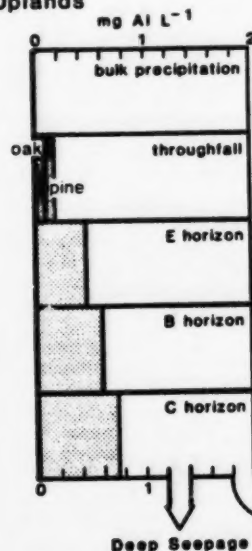
Forest Floor

Forest floor samples, eight upland and five pine lowland, were taken by cutting out 15- by 15-cm blocks that extended down to mineral soil (1 to 8 cm). The Oi (litter, O1) and Oe and Oa (fermented and humic, O2) horizons were separated for analysis. The samples were oven dried (70°C), ground, and ashed using the same procedure as for tissue samples, except that 2 g of each sample were ashed.

Mineral Soil

Volumetric mineral-soil samples (250-cm³ cores) were obtained at 10-cm intervals to a depth of 1 m from three soil pits and at 25-cm intervals to a depth of 2 m from a fourth pit. Samples were air dried and screened through a 2-mm mesh stainless steel sieve. Bulk density was calculated for the < 2-mm fraction (by subtracting the mass and volume of the > 2-mm fraction [1 to 15% of the total sample]). Soil-pool data, thus, are reported for the < 2-mm size fraction.

Uplands



Aluminum content of the soil was measured using three soil extraction procedures slightly modified from Perkin-Elmer (1971): (i) "exchangeable" Al was extracted using a 1 M solution of ammonium acetate, acidified to pH 4.5 with HCl; (ii) double-acid "extractable" Al was measured using a 0.075 M mixture (0.05 M HCl + 0.025 M H₂SO₄); and (iii) total Al concentration was determined using an HF-HCl digestion procedure.

Sample Collection-Analysis

Bulk precipitation, stream, and lowland pore-water samples were collected at weekly to monthly intervals from May 1978 to January 1982. Lysimeter and throughfall sampling followed the same schedule beginning in the fall of 1979. Tissue, forest floor, and soil samples were obtained in the summer and fall of 1980.

The pH of water samples was determined in the laboratory within 1 to 24 h by glass electrode. Lowland pore-water samples were passed through a 1-μm membrane filter, but other samples, which appeared clear, were not filtered. No difference in trace metal chemistry was observed between filtered and unfiltered samples (Swanson, 1979). All samples were acidified with Ultrex HNO₃ (10 mL L⁻¹) to prevent changes in concentration during storage. Dissolved-organic content was estimated using a colorimetric procedure suggested by Gjessing (1976) in which absorbance of the acidified samples was measured at 430 nm using a deionized water blank. The colorimetric measurements correlated strongly with dissolved organic carbon ($r = 0.827$, $P < 0.001$, $n = 22$).

Concentration of Al was determined on a Jarrel Ash inductively coupled, plasma-emission spectrophotometer (ICP) at the Soil Testing and Plant Analysis Laboratory, Univ. of Georgia, Athens. Analytical accuracy was verified by comparing analyses of known standards and samples having known spikes on both the ICP unit in Georgia and on a Perkin-Elmer graphite-furnace atomic absorption spectrophotometer at the Univ. of Pennsylvania, Philadelphia.

RESULTS AND DISCUSSION

Aluminum in Solution

Figure 1 summarizes the volume-weighted concentrations of Al measured in water flowing through the forest ecosystem.

Precipitation and Throughfall

The volume-weighted mean concentration of Al in bulk precipitation was 0.012 mg L⁻¹ (see Table 1). No

Lowlands

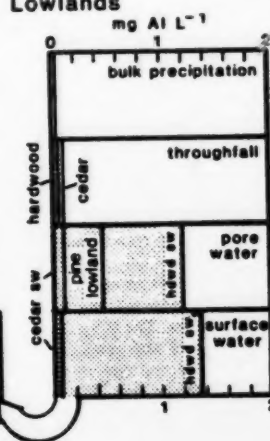


Fig. 1. Mean volume-weighted concentrations of Al in water moving through the McDonalds Branch watershed, November 1979 to January 1982.

trends in Al concentration in precipitation were observed. Aluminum concentration did not correlate with pH or amount of precipitation.

The observed mean in this study was low compared with bulk-precipitation values of 0.19 mg L⁻¹ observed by Heinrichs and Mayer (1977) on the Solling Plateau in Germany and 0.03 mg L⁻¹ measured by Ugolini et al. (1977) at Findley Lake in Washington. The McDonalds Branch mean concentration was similar to the 0.018 mg L⁻¹ reported by Cronan (1980) for a subalpine zone in New Hampshire, and a wet-precipitation value of 0.008 mg L⁻¹ measured by Liljestrand and Morgan (1978) in Pasadena, CA.

Throughfall in the McDonalds Branch basin was enriched considerably in Al relative to precipitation and had a volume-weighted mean upland (pine and oak) Al concentration of 0.14 mg L⁻¹. Throughfall Al concentration was related inversely to amount of precipitation ($r = -0.43$, $P < 0.015$). Aluminum concentration was highest in throughfall under shortleaf pine and lowest under the red maple-black gum hardwood-swamp foliage (Table 1).

Throughfall Al concentration was correlated inversely ($r = -0.35$, $P < 0.05$) with throughfall pH under the upland pine and oak, but not under the lowland species. In both uplands and lowlands, Al in throughfall under the conifers was higher than under the hardwoods. This suggests that conifers lost more Al from their foliage or that they were more efficient at scavenging particulate Al from the atmosphere. Seasonal trends in Al concentrations were not observed under either deciduous or evergreen trees.

The mean throughfall Al concentration at McDonalds Branch was four times the mean at Findley Lake under Pacific silver fir (*Abies amabilis*, 0.03 mg L⁻¹ [Ugolini et al., 1977]), nearly three times the mean under Mt. Moosilauke balsam fir (*A. balsamea* Mill., 0.045 mg L⁻¹ [Cronan, 1980]), but less than one half of the means under the Solling beech and spruce (*Picea abies* Karst., 0.31 and 0.50 mg L⁻¹ [Heinrichs and Mayer, 1977]). From the available data, it is unclear to what extent these differences resulted from differences in Al deposition at each location or from variations in Al leaching from the vegetation.

Soil Water

Volume-weighted mean Al concentrations and ranges for each lysimeter type and depth are given in Table 2. Aluminum concentrations in soil solution of the sandy soils of the McDonalds Branch watershed showed great

Table 1. Mean volume-weighted Al concentrations and pH for bulk precipitation and throughfall in the McDonalds Branch watershed from November 1979 to January 1982.

	Al			pH	
	Mean	Range	n	Mean	Range
	mg L ⁻¹				
Bulk precipitation	0.012	0.000-0.238	34	4.1	3.6-4.5
Throughfall					
Oak-pine average	0.139	0.053-0.499	33	3.8	3.4-4.1
Oak	0.095	0.018-0.265	33	3.8	3.4-4.2
Pine	0.182	0.073-0.787	32	3.8	3.5-4.2
White cedar	0.102	0.010-0.301	13	4.0	3.5-4.5
Black gum/red maple	0.046	0.014-0.119	13	4.3	3.9-5.0

spatial and temporal variability. Significant variability in Al concentration also was evident among the different types of lysimeters (Turner, 1983). The cause may have been differential collection efficiency of the various lysimeter types under different soil moisture conditions. However, laboratory leaches of each lysimeter type with acidified (pH 4), deionized water showed that the aluminum oxide, aluminum-plate tension lysimeters contaminated solution passing through them with Al and increased the solution pH by 0.5 unit (Turner, 1983). Samples from tension lysimeters at all depths in the field had up to 3 times higher Al concentrations and up to 1.5 unit higher pH than the other two lysimeter types (Table 2). Not all of this difference was due to contamination, however. Some unknown amount was due to different fractions of water sampled by the different lysimeter types. In these acid soils, the tension lysimeter Al data probably accurately represent trends in Al concentration over time, but the Al values are too high by some unknown percentage. The Al values from the tension lysimeters were, therefore, not included in the overall means or in the budget calculations below, though they were used for interpretation of biogeochemical controls on Al mobility in the soils.

Temporal trends in Al concentrations at each soil depth are shown in Fig. 2. The general pattern for all lysimeters and soil depths showed high Al concentrations in late winter and spring and lowest concentrations in the summer and fall. Minimum Al concentrations were measured in the summer of 1980, which was a drought period.

Possible biogeochemical controls on Al concentrations in the soil solution include precipitation pH, throughfall pH and Al concentration, pH of the soil solution, amount of moisture in the soil, amount of dissolved organic matter in solution, and amount of biological activity releasing organically bound Al from litter (moisture and temperature controlled).

Table 2. Mean volume-weighted aluminum concentrations, DOM (dissolved organic matter) as absorbance, and pH for lysimeter samples from E, B, and C soil horizons and at 200-cm depth.

	Al			n	DOM		pH	
	Mean	Range	Mean		Range	Mean	Range	
	— mg L ⁻¹ —							
E horizon (10 cm)								
Tension	1.131	0.300-6.190	201	0.52	0.08-2.0	4.3	3.5-6.7	
0-Tension	0.606	0.021-3.200	186	0.38	0.08-2.0	3.9	3.3-4.9	
Funnel	0.298	0.059-0.879	50	0.31	0.14-0.74	3.6	3.2-3.9	
Mean E†	0.452	± 0.154		0.35	± 0.03	3.8	± 0.1	
B horizon (30 cm)								
Tension	0.940	0.221-3.908	207	0.27	0.01-1.7	4.2	3.4-5.6	
0-Tension	0.493	0.091-1.255	66	0.21	0.02-0.43	3.9	3.3-4.3	
Funnel	0.715	0.179-1.532	46	0.23	0.03-0.69	3.6	3.2-4.0	
Mean B†	0.604	± 0.111		0.22	± 0.01	3.8	± 0.1	
C horizon (100 cm)								
Tension	0.972	0.074-2.426	202	0.01	0.0-0.05	4.5	3.8-5.6	
0-Tension	0.762	0.093-2.171	14	0.01	0.00-0.04	4.2	3.7-5.1	
Funnel	0.694	0.533-1.859	21	0.00	0.00-0.03	3.9	3.7-4.3	
Mean C†	0.728	± 0.034		0.01	± 0.01	4.0	± 0.1	
200 cm	0.3	0.140-0.434	13	0.00	0.00-0.02	4.0	3.7-4.2	

† Means do not include tension-lysimeter values.

Aluminum concentrations in E horizon lysimeters were correlated positively with the dissolved organic carbon content of the soil solution (Fig. 3) and correlated inversely with soil temperature. Aluminum apparently was flushed from the forest floor in association with mobile organic matter during the winter and spring, when soil moisture was high.

For data pooled from all B horizon lysimeters, B horizon Al concentrations were not correlated strongly with any of the measured parameters except temperature (an inverse correlation). However, Al in individual lysimeters often was correlated with dissolved organic matter, pH (an inverse correlation), or volume collected. That is, Al in some B horizon lysimeters behaved

similarly to Al in the E horizon (associated with dissolved organic matter), while Al in other B horizon lysimeters behaved like Al in C horizon soils. Organic matter disappeared from solution by the time it reached some B horizon lysimeters and all C horizon lysimeters. A B2h soil horizon was very faint and discontinuous in these soils, and did not show up in chemical analyses of the soils.

Total Al in C horizon solution correlated inversely with pH and directly with volume collected. The concentration of dissolved organic matter was very low in the C horizon solution, and Al concentration apparently depended upon pH and soil-solution amounts. Figure 4 shows the relationship between total Al and pH of the C horizon solution and the solubility of gibbsite. The data shown are all from tension lysimeters. Most samples fall close to the predicted solubility curve. Undersaturated samples to the left of the curve were collected after heavy rain or during relatively wet periods when equilibrium probably was not reached because of rapid percolation rates. Leachates from zero-tension and funnel lysimeters represented mainly saturated flow through the soil and were all undersaturated with Al. Many samples in Fig. 4 appear to be supersaturated, especially at higher pH, perhaps due to contamination of the solution as it passed through the aluminum plate, to disequilibrium caused by slow rates of gibbsite precipitation, or

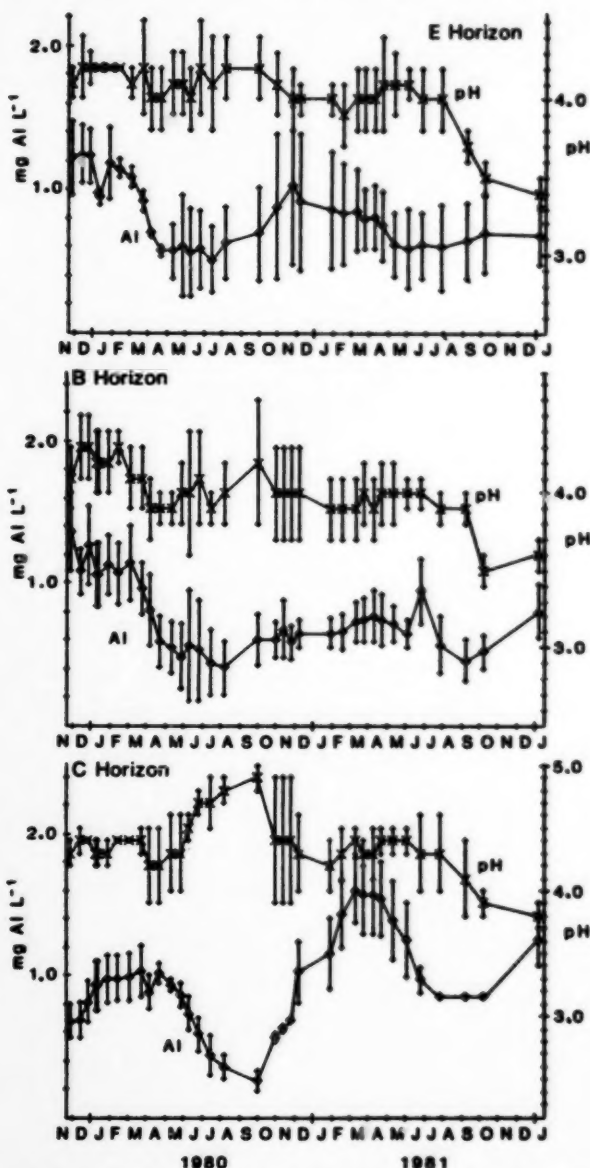


Fig. 2. Temporal trends in mean soil-solution Al concentration and pH for E, B, and C horizons. Bars represent standard error of the mean of the three lysimeter types, for each collection period.

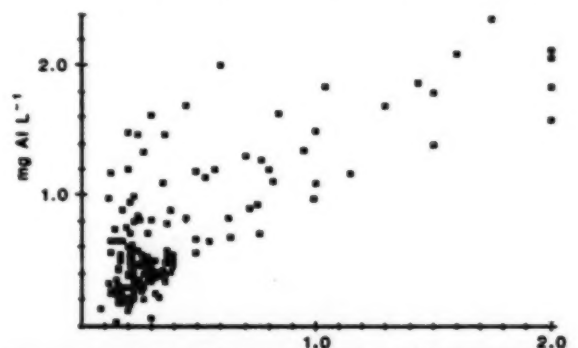


Fig. 3. E horizon, soil-solution Al concentration vs. dissolved organic matter as absorbance.

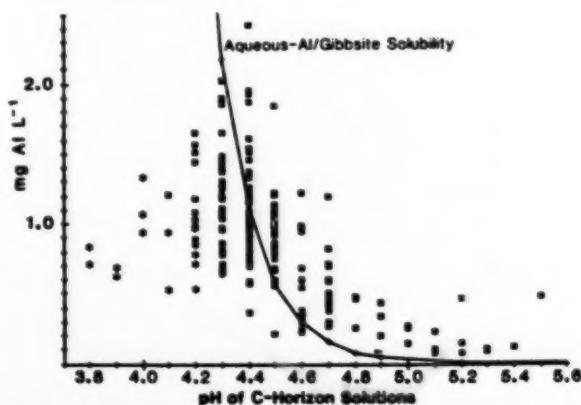


Fig. 4. C-horizon, soil solution Al concentration vs. pH. Samples designated "•" were collected during wet periods and were of large volumes. Gibbsite solubility data is from May et al. (1979).

as a result of complexation (e.g., with organics, fluoride, hydroxide, sulfate, or silicate).

The biogeochemical controls on H^+ concentration in soil solution are important because of the potential role of H^+ in Al solubility. The pH in E horizon soil solution correlated inversely with the amount of precipitation and leachate collected. In some cases, the pH of the E solution correlated with throughfall pH. In the B and C horizons, solution pH correlated with the pH of water percolating from above and correlated inversely with the amount of water moving through the soil. Because precipitation pH and volume did not correlate ($r = -0.1547$, $P < 0.39$), internal soil processes appear to have controlled H^+ concentration in the soil solution (Bache, 1980; Ulrich, 1980; Ulrich et al., 1980). Those atmospheric H^+ ions that were conserved through these processes, and any internally generated H^+ ions, were flushed through the soil profile during periods of higher moisture flux.

Aluminum (Al^{3+}) and H^+ (and other cations) in solution must be balanced by anions on an equivalent weight basis. The atmospheric contribution of H^+ to the Pine Barrens ecosystem was found by Means et al. (1981) to be accompanied by more than twice as much SO_4^{2-} (on an equivalent-weight basis). Pine Barrens streams exported about two-thirds of the SO_4^{2-} input in precipitation. However, Means et al. found that the maximum concentrations of SO_4^{2-} in the streams occurred in the winter, although the maximum SO_4^{2-} concentrations in precipitation occurred in the summer. SO_4^{2-} was mobile in the soils but had a lag time of roughly 0.5 yr that resulted in a seasonal pattern that corresponded with the seasonally high moisture flux, low pH and high Al concentrations found in this study. SO_4^{2-} apparently was effectively adsorbed by the soils during the summer when precipitation concentrations were higher and when soil solution concentrations were increased by evapotranspiration (SO_4^{2-} adsorption is a concentration-dependent process). During winter, with lower SO_4^{2-} input concentrations and greater soil moisture fluxes, SO_4^{2-} desorption occurred. Thus, soil moisture flux may be a surrogate measure for SO_4^{2-} mobility in these soils.

The above data and relationships support the following model for Al mobility in these acidic, sandy soils. Aluminum concentrations in upper soil horizons (O, E, and upper B) were controlled in part by leaching, breakdown, and dissolution of organic matter. Also, the very acidic solution in the upper horizons released Al from exchange sites and dissolved Al from gibbsite and Al-interlayered clays. Aluminum thus moved as organic Al complexes, as aqueous Al^{3+} ions (and lesser amounts of other inorganic Al species), and inorganic Al complexes. The organic matter was oxidized or metabolized by soil organisms in the B horizons. Aqueous Al^{3+} (primary species at this pH), balanced by SO_4^{2-} , moved from where it was released from the organic complex to the soil depth where pH was high enough for sorption of Al on exchange sites or for precipitation of gibbsite or similar $Al(OH)_3$ mineral. This depth was deeper in the soil profile during the winter and spring, when large fluxes of the acidic water (with mobile SO_4^{2-}) occurred, but was higher in the profile in the summer and fall when water fluxes (and SO_4^{2-} mobility) were less. Aluminum concentrations in lower-horizon solutions thus

were dependent on solution pH through ion exchange and solubility of gibbsite or similar minerals (plus any organic or inorganic complexes present). Solution pH was dependent on SO_4^{2-} concentrations which depended on soil moisture flux. Therefore, the flushing during wet periods of organically and inorganically complexed Al, internally produced H^+ , and atmospherically deposited H_2SO_4 was responsible for total Al fluxes through the upland soils.

Soil-solution pH and Al concentrations were not related to precipitation pH on an event or seasonal basis because of soil processes such as ion exchange, SO_4^{2-} absorption, biological H^+ production, and seasonal changes in soil-moisture status. Acid precipitation may, however, be causing a long-term increase in Al concentrations and mobility in this ecosystem because of increased loading of H_2SO_4 .

Aluminum concentrations in the lowland-soil pore water are shown in Table 3. Seasonal patterns of pine-lowland samples were similar to upland C-horizon samples. However, Al concentrations in lowland samples may have been somewhat lower than in upland C horizon samples because of Al retention in the distinct B2hr horizon present in the low-lying Lakehurst soils. Lowland Al concentrations correlated positively with precipitation input and inversely with soil solution pH. Thus, Al concentrations in the pine-lowland Lakehurst sands probably were subject to the same geochemical controls as the upland soils, except that some Al apparently was retained in the lowland B2hr horizon.

Aluminum concentrations in the cedar-swamp pore water (Table 3) were very low compared with all other soil and stream values and even were below cedar-swamp throughfall concentrations. Aluminum values did not correlate significantly with any other factors, though cedar-swamp pore water pH was quite high and relatively constant. Total Al in these samples was undersaturated relative to gibbsite solubility, probably because of complexation of Al by insoluble, immobile organic matter in the bog soils.

Aluminum values in hardwood-swamp pore water were, on the other hand, among the highest Al values measured (Table 3). They correlated strongly with dissolved organic matter and were highest in summer, when the water contained the most dissolved humus.

There are relatively few published data on Al in forest soil solutions and its relationship to other soil factors. Heinrichs and Mayer (1977) reported mean Al concentrations of 0.56 and 1.70 mg L^{-1} and 1.10 and 1.90 mg L^{-1} for seepage below humus layer and seepage below 50 cm in beech and spruce forests, respectively. Aluminum levels in solution in the highly leached McDonalds

Table 3. Mean aluminum concentrations, DOM (dissolved organic matter) as absorbance, and pH for lowland pore water samples.

	Al		n	DOM		pH	
	Mean	Range		Mean	Range	Mean	Range
	— mg L^{-1} —			—			
Pine lowland	0.454	0.116–0.876	16	0.06	0.01–0.17	4.3	3.4–4.6
Cedar swamp	0.087	0.035–0.152	16	0.03	0.01–0.08	4.6	4.5–4.8
Gum/maple swamp	1.200	0.527–3.170	15	0.57	0.05–2.0	3.7	3.3–4.0

Branch soils generally were lower than for the loess-derived Solling soils. Ugolini et al. (1977) reported Al values generally comparable in magnitude to the Pine Barrens data, although the pH values of Washington subalpine soil solution were about one unit higher. In the Ugolini study, Al concentration was inversely related to pH in the upper horizons and decreased from 0.75 mg L⁻¹ beneath the O horizon to 0.35 mg L⁻¹ in the B2hr horizon but increased again with depth as pH also increased. Cronan (1980) also found similar Al concentrations in percolate below the forest floor (0.5 mg L⁻¹) and values as high as 1 mg L⁻¹ in the B2 horizon.

Ulrich et al. (1980) presented Al data for an equilibrium soil solution for April 1969 to November 1969 that showed a late summer peak followed by an October decline and a November maximum. Tyler (1981) reported detailed seasonal data for Al in lysimeter percolate from below the forest floor that showed distinct maxima in late summer and fall over a 2-yr period. He also showed that Al concentration correlated strongly with dissolved organic matter, which was abundant in soil solution during warm, moist, summer and fall periods. Thus, for the several systems for which time-series data have been reported, Al concentrations appear to be ultimately dependent on high soil moisture flux and internal soil processes, at least in the short term, independent of precipitation pH.

Stream and Groundwater

Streamflow in McDonalds Branch is a mixture of (i) groundwater derived from flow through the upland and lowland mineral soils and (ii) pore water and surface water from the hardwood and cedar swamps. Stream water Al concentrations, therefore, reflected the mixing of those waters.

McDonalds Branch stream water had a volume weighted mean total Al concentration of 0.15 mg L⁻¹ (Table 4). Surface water within the cedar swamp averaged 0.065 mg L⁻¹, whereas water flowing through the hardwood swamp in the upper reaches of the watershed ranged from 0.90 to 2.12 mg L⁻¹, with a mean of 1.35 mg L⁻¹.

In stream water, total Al, discharge, dissolved organic matter, and pH were highly intercorrelated. Neither partial correlations nor multiple regressions could be used with confidence to assess the importance of one factor over another in controlling Al concentrations (Turner, 1983). Stream Al was undersaturated relative to gibbsite solubility, probably because of complexation of Al by immobile organic matter as the stream flowed

through the cedar swamp. Stream Al concentrations correlated with amount of precipitation but did not correlate with precipitation pH.

Figure 5 shows total Al concentration in the stream water during the study. When stream levels were high (1978-1979) and significant drainage from the hardwood swamp and upper horizons of the pine lowland soils occurred (low pH and high dissolved organic concentrations), Al concentrations were high. However, Al concentrations generally were low, during the reduced flow periods of the summer and fall months (e.g., 1978) and drought periods (1980-1981, high pH and low dissolved organic concentrations). Superimposed on these patterns were very high stream Al concentrations following large rainfall events or unusually wet periods. These high values reflected rapid flushing of accumulated acids and Al through the upland, lowland, and bog soils, probably bypassing the deep upland soils.

Aluminum concentrations observed in McDonalds Branch were considerably higher than those reported for "average stream waters" (0.01 mg L⁻¹ [Stumm and Morgan, 1970]). They were similar to or higher than concentrations of Al measured in other acidified streams.

Falls Brook (in the Hubbard Brook watershed) had a mean total Al concentration of 0.71 mg L⁻¹ at the highest elevation sampling station. Several hundred meters downstream, Al concentration fell to 0.32 mg L⁻¹. About 2.5 km downstream, at the confluence with Hubbard Brook, Al measured 0.15 mg L⁻¹ (Johnson et al., 1981). By comparison, Al concentration in McDonalds Branch at the headwaters and 2.5 km downstream at the USGS weir was 1.35 mg L⁻¹ and 0.21 mg L⁻¹, respectively.

Means et al. (1981) reported total Al concentrations for higher-order Pine Barrens streams (Cedar Creek, Mullica River) ranging from 0.05 to 0.3 mg L⁻¹. In high elevation Adirondack streams and lakes having pH < 5, Al concentrations ranged from 0.1 to 1.0 mg L⁻¹ (Schofield, 1976; 1977).

Groundwater output of Al was not measured in this study. Low flow stream Al values (0.1 mg L⁻¹) may underestimate mean groundwater Al concentrations be-

Table 4. Mean volume-weighted aluminum concentrations, DOM (dissolved organic matter) as absorbance, and pH for McDonalds Branch stream water collected above the USGS weir, and arithmetic-mean Al, DOM, and pH for swamp surface waters.

	Al		n	DOM			pH	
	Mean	Range		Mean	Range		Mean	Range
	mg L ⁻¹							
	Stream							
11/79-1/82	0.147	0.014-0.502	36	0.04	0.01-0.12	4.1	3.4-4.5	
5/78-1/82	0.206	0.014-0.502	92	0.08	0.01-0.51	4.0	3.2-4.5	
Swamp surface water (January 1981-January 1982)								
Cedar	0.065	0.001-0.117	11	0.06	0.03-0.12	4.4	4.2-4.7	
Gum/maple	1.345	0.899-2.123	8	0.23	0.08-0.64	3.6	3.5-3.7	

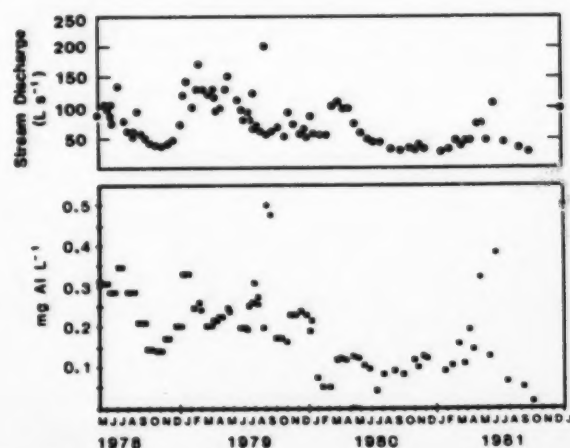


Fig. 5. Stream water Al concentrations and stream discharge from May 1978 to January 1982. Samples designated "•••" were taken during wet periods or after heavy rains.

cause of immobilization of Al in the cedar swamp. Two-meter upland lysimeter values (0.3 mg L^{-1}) may be a better estimate. However, Means et al. (1981) reported Pine Barrens groundwater Al concentrations ranging from 0.2 to 5.0 mg L^{-1} , with a mean of 1.96 mg L^{-1} . Rhodehamel (1970) cited a range of 0.0 to 10 mg L^{-1} for Pine Barrens wells, with 1.0 mg L^{-1} as a more common maximum value. These values compare with the 0.6 mg Al L^{-1} determined by Cronan (1980) for spring water on Mt. Moosilauke, NH.

Aluminum in Storage

Data on pools of Al in vegetation, forest floor, and soil are summarized in Fig. 6. The upland subsystem is emphasized because, as a result of lateral flows, determination of water budgets for the lowland subsystems was beyond the scope of this study.

Vegetation Pool

The standing pool of Al in vegetation was compartmentalized by tree species and tree parts, plus shrubs. Measured concentrations (Table 5) followed the pattern: bark > leaves and twigs > wood, for all species. It is unclear whether this represents a physiological distribution of Al or results from impaction and retention of airborne Al by the bark, leaves, and twigs.

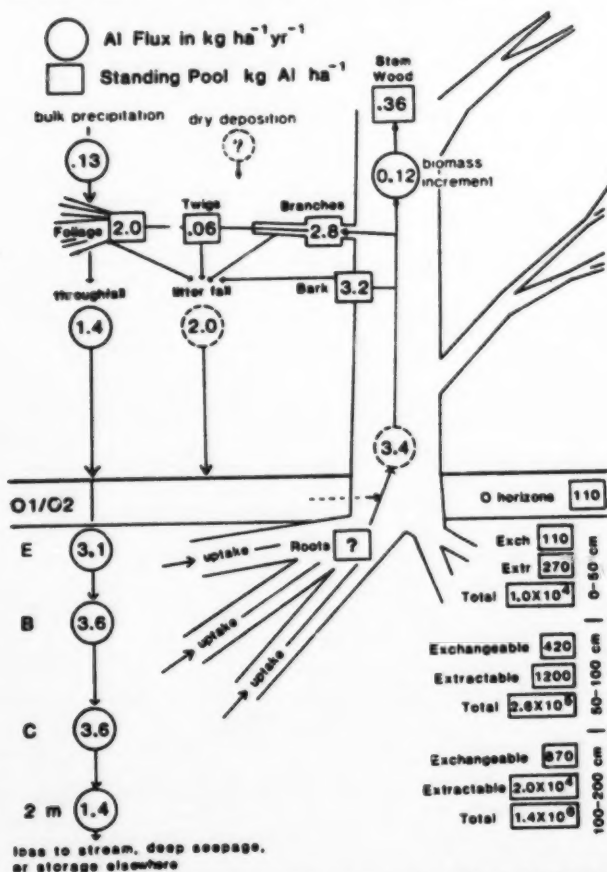


Fig. 6. Aluminum standing pools and measured or estimated (dashed circles) annual fluxes in the Pine Barrens upland ecosystem.

Fine roots contained two to three orders of magnitude more Al than any other tissue. This may be because of the Al incorporated into the tissue or because of the difficulty of separating the root tissue completely from soil. For these reasons, and because it is very difficult to distinguish the species of roots in a mixed stand, root pools are unknown.

Pines had higher Al concentrations than the oaks in the upland ecosystem. The shrubs (mostly ericaceous) also were relatively high in Al. Bowen (1979) reported a range of 90 to 530 mg kg^{-1} Al for land plants, the Ericaceae being Al accumulators. Chenery and Sporne (1976) indicated that most plant leaves contain less than 300 mg kg^{-1} Al, and Hutchinson (1945) reported an average of 20 mg kg^{-1} for whole living plants. Thus, Al concentrations in McDonalds Branch vegetation were near the upper end of the range for Al in plants.

Figure 6 shows the distribution of Al in McDonalds Branch upland vegetation. Bark and branches accounted for a large percentage of the Al associated with vegetation. Leaves and twigs also contained large amounts of Al, considering they comprised only 8% of the total biomass.

Forest-Floor Pool

Large quantities of Al were found in both Oi (O1) and Oe/Oa (O2) horizons. Aluminum concentration in the Oi was $1.0 \pm 0.1 \text{ g kg}^{-1}$, three to four times the Al concentration in tree leaves. Aluminum concentration in the upland Oe/Oa horizon was $1.2 \pm 0.1 \text{ g kg}^{-1}$ and twice that high in the lowland Oe/Oa horizons. On an area basis, more than 10 times as much Al was in the upland organic forest floor as in the standing biomass.

Mineral-Soil Pool

As expected, the mineral soil contained by far the most Al. Figure 7 shows soil Al concentrations by depth for ammonium acetate exchangeable, double-acid extractable, and total Al. Exchangeable and extractable Al

Table 5. Mean Al concentrations for upland vegetation. $N = 2$ to 10 , depending on the compartment.†

	Pitch pine	Short-leaf pine	Black oak	White oak	Black-jack oak	Shrubs
	mg/kg dry wt					
Stemwood	12 (2)‡	15 (0.1)	7.3‡ (1.8)	8.5 (0.7)	7.3‡ (1.8)	
Stembark	670 (40)	490 (30)	111‡ (20)	77 (20)	111‡ (20)	
Branches	283 (68)	233 (88)	25 (3)	74 (21)	27 (2)	
Twigs	235 (6)	218 (59)	38‡ (4)	38‡ (4)	38‡ (4)	
New leaves	356 (23)	428 (61)	50‡ (8)	64 (16)	50‡ (8)	
Old leaves	600 (38)	753 (49)				
Aboveground Total						118 (5)

† Al concentrations for shortleaf pine fine roots collected from E and B/C soil horizons were 2900 ± 200 and $4400 \pm 400 \text{ mg/kg}$, respectively ($N = 14$ for each horizon).

‡ Pooled data

§ Standard error in parentheses.

represent a pool of Al that might be mobilized under short-term natural conditions. Total Al includes available Al plus that bound in mineral structures, probably labile only after long-term weathering. Aluminum amounts in these profiles correspond with amounts of gibbsite, kaolinite, and Al-interlayered vermiculite and smectite in profiles for Lakehurst soils reported by Douglas and Trela (1979). The large soil concentrations of Al at 125 to 150 cm are consistent with the large solution concentrations of Al at the 1-m lysimeter depth and the much lower leachate concentrations measured at 2-m depth.

The highly leached sandy soils at McDonalds Branch were very low in total aluminum ($< 10 \text{ g kg}^{-1}$) compared with soils elsewhere. Bowen (1979) reported a mean of 71 g kg^{-1} Al in soils of the world. The loess-derived Solling (FRG) soils ranged from 36 to 46 g kg^{-1} Al (Heinrichs and Mayer, 1977). The aluminum remaining in the highly weathered New Jersey Pinelands soils probably is associated mainly with resistant secondary soil minerals rather than with more readily weatherable primary minerals such as are found in most other soils.

Aluminum Fluxes and Budget

Measured and estimated annual fluxes of Al through the upland ecosystem are shown in Fig. 6. Recognizing that some of the fluxes in the system (dry deposition, litterfall, vegetation uptake) are rough estimates, the diagram suggests which compartments within the system may have been sources or sinks of labile aluminum.

Small net gains of Al were apparent in vegetation and forest-floor compartments. A net increment of $0.12 \text{ kg ha}^{-1} \text{ yr}^{-1}$ to the aboveground biomass was measured based on growth-rate and tissue-chemistry data. Inputs of $3.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$ to the forest floor included throughfall ($1.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$) plus litterfall ($2.0 \text{ kg ha}^{-1} \text{ yr}^{-1}$, estimated from amounts in foliage, twigs, and bark) plus an unknown additional amount from dry deposition (assumed for these calculations to be near 0). Movement

of Al out of the forest floor through the E horizon was $3.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Subtracting outputs from inputs shows a small net annual gain of Al by the forest floor. The forest floor must have a long-term net gain of Al or a balance of Al input/output to accumulate and maintain the large standing pool present.

Net Al movement in the mineral soil was from upper to lower horizons, or beyond. Aluminum input to the mineral soil was $3.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ from the forest floor. To supply the Al in throughfall and litterfall, vegetation had to take up an approximately equivalent amount, or slightly more, from the soil, depending on how much of the throughfall Al was leached from the foliage (derived from the soil) and how much was derived from the atmosphere (dry deposition). The depths from which vegetation uptake took place are unknown. A total of $3.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of Al was transported below the 1-m C horizon soil depth, $1.4 \text{ kg Al ha}^{-1} \text{ yr}^{-1}$ passed the 2-m depth, and only $0.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$ was exported in the stream. It appears, therefore, that Al was transported from upper soil horizons and redeposited below 1-m depth or exported in ground and stream water.

SUMMARY

Aluminum in the McDonalds Branch basin was partitioned strongly into the lower mineral-soil horizons. Large stores of potentially labile Al were found in the mineral soil, forest floor, and foliage. Although standing vegetation represented a relatively small pool of Al, it cycled substantial amounts of Al between mineral soil and the forest floor (approximately 40% of standing biomass pool per year; 3% of forest floor pool). Aluminum transport from the forest floor into E and B mineral-soil horizons occurred in association with wet season fluxes of organic acids and atmospheric sulfuric acid. In the B horizon, organic matter was oxidized or metabolized by soil organisms. Aluminum mobility through the B and C horizons was dependent on the flux of soil moisture and the concentration of inorganic acids. Distinct seasonal Al fluxes, independent of pre-

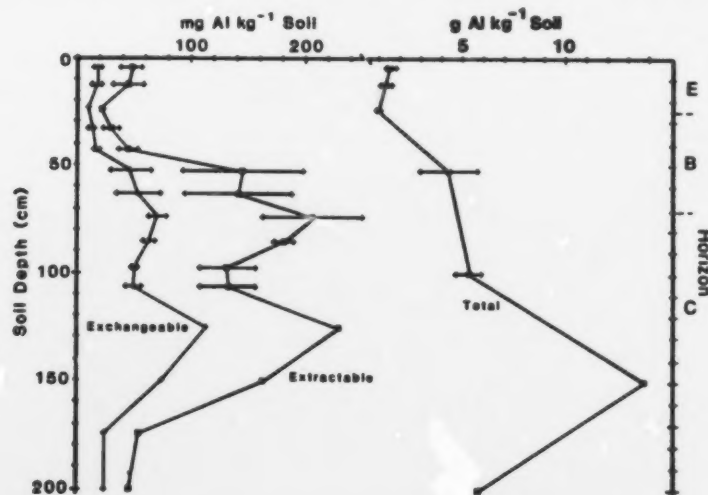


Fig. 7. Mineral-soil Al concentrations in upland (Lakewood) soils. Bars represent standard error of the mean of samples from four pits. Samples below 110 cm are from one pit only.

cipitation pH patterns, occurred with fluxes of internally produced acids and atmospherically deposited sulfuric acid that were flushed through the soil during the wet winter and spring seasons. Aluminum movement occurred to the depth (zone) in the soil at which H^+ ion was exhausted by exchange site sorption and dissolution of gibbsite (or other Al-bearing minerals) below which Al concentration in solution decreased because of Al sorption on exchange sites and gibbsite redeposition.

Aluminum output via the stream was dependent on complex interactions between shallow groundwater baseflow to the stream and fluxes within and through the pine lowlands and swamps. Cedar-swamp and pine-lowland waters had relatively low concentrations of Al, probably because of complexation of Al by immobile organic matter. Aluminum concentrations in the hardwood swamp were very high and were correlated strongly with mobile, dissolved organic matter. Summertime seasonal maxima of Al in the hardwood swamp did not correspond with wintertime seasonal maxima of Al fluxes through the C horizon into shallow groundwater baseflow. The relative contributions of Al to the stream by baseflow and swamp waters/upper mineral horizons depended on stream level in which high flow periods had high Al and dissolved organic matter concentrations and low pH.

Aluminum output in deep seepage was dependent on lower soil horizon geochemistry and soil moisture flux, and periods of high flux had higher Al concentrations.

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